SUPERCRITICAL WATER GASIFICATION OF COAL USING $CA(OH)_2$ AS AN ADDITIVE

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ABSTRACT

A few coals were gasified under the supercritical water conditions in an autoclave at a temperature up to 700 °C and a pressure up to 30 Mpa. Calcium hydroxide was used both as a catalyst and an absorbent for the capture of CO_2. The carbon conversion, gas and liquid productions, CO_2 sorption by calcium and calcium utilization were determined in the experiments. Without the addition of Ca, the carbon conversion of Yallourn coal was about 44% at 690 °C and 28 Mpa; whereas the addition of Ca up to a Ca/C molar ratio of 0.6, the carbon conversion increased by 22%. Correspondingly, hydrogen yield was increased from 0.23 to 0.37 NL/g-coal (daf), methane yield from 0.16 to 0.19 NL/g-coal(daf), and ethane yield from 0.015 to 0.03 NL/g-coal(daf). At a Ca/C ratio of 0.6, almost no CO_2 remained in gas phase, with a calcium utilization value of 50-60%.

INTRODUCTION

Gasification is one of the oldest coal utilization processes. The present paper is concerned with the gasification of coal in supercritical water at a temperature up to 700 •C and a pressure around 30 Mpa with the addition of calcium hydroxide. The essential idea concerning this research subject has been proposed by Lin et al [1]. They found that when several coals were gasified in supercritical water at temperatures 650-700 °C and a pressure of 60 Mpa using lime and a small amount of sodium compounds as additives, very high carbon conversion could be achieved with a high proportion of hydrogen and some CH_4 and CO in resultant gas. The following global reactions are principally taken into account in the gasification system:

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H_{900} = 140.3 \text{ kJ mol}^{-1} \quad (1)$$
$$H_2O + CO \leftrightarrow CO_2 + H_2 \quad \Delta H_{900} = -32.6 \text{ kJ mol}^{-1} \quad (2)$$
$$Ca(OH)_2 \leftrightarrow CaO + H_2O \quad \Delta H_{900} = 92.6 \text{ kJ mol}^{-1} \quad (3)$$
$$CO_2 + Ca(OH)_2 \leftrightarrow CaCO_3 + H_2O \quad \Delta H_{900} = -83.4 \text{ kJ mol}^{-1} \quad (4)$$
$$CO_2 + CaO \leftrightarrow CaCO_3 \quad \Delta H_{900} = -176.0 \text{ kJ mol}^{-1} \quad (5)$$

Where the values of reaction heat change refers to those at a temperature of 900 K, a steam pressure of 30 Mpa and other gas pressures of 0.1 Mpa. As shown in reactions (4) and (5), lime or slaked lime can also play an important role in capturing environmentally unfriendly CO_2 and sulfur-bearing gases. As the released CO_2 gas is eliminated effectively by $Ca(OH)_2$ and/or CaO by reactions (4) and (5), CO can thus be highly transferred to hydrogen by enhancing the forward step of reaction (2).

In the present study, we aim at revealing catalytic effect of calcium hydroxide on supercritical water gasification of coal because no meticulous report has been documented regarding this interesting issue. We also would like to discuss the behaviors of calcium hydroxide for the retention of CO_2 in supercritical water.

EXPERIMENTAL

Gasification was carried out in a 20 ml batch autoclave. In each run, a 0.2 g sample of coal mixed with the desired amount of $Ca(OH)_2$ was added into the reactor with the injection of around 3.5 ml distilled water. It typically took 20 min for temperature to rise from room temperature to 690 °C.

Compositional analysis of the resultant gas was carried on a gas chromatograph, which used molecular sieve column in one channel and HaySep A column in another with TCD detectors (detectable gasses: H_2, O_2, N_2, CH_4, CO, CO_2, C_2, C_3 and C_4). The reacted slurry was filtered to collect the liquid. Some of the filtrates were analyzed on a gas chromatograph to determine BTX, PCX and naphthalene. Effort was made to collect the solid with least loss. The solid was dried at 107 °C in flowing nitrogen and then subjected to the analysis of the forms of carbon in it (total carbon content and carbon content as $CaCO_3$) through a method of acid dissolution.

Reagent-grade calcium hydroxide was purchased from Wako Co. in Japan. Table 1 lists the characteristics of coal samples used in the study. The particle size of coal samples was screened between 60 and 100 Tyler mesh.

Table 1. Characteristics of Coal Samples used in the Study

Coal sample	Proximate analysis (wt%, as-received)				Ultimate analysis (wt%, daf)				
	Moisture	VM	Ash	FC	C	H	N	S	O
Yalloum (YL)	14.3	47.3	0.8	36.6	66.1	5.3	0.6	0.3	27.7
Morwell (ML)	10.0	46.3	1.4	43.3	67.9	5.0	0.5	0.3	26.3
Tanitoharum (TN)	4.6	48.8	5.0	41.6	76.3	5.6	1.4	0.2	16.5

RESULTS AND DISCUSSION

Table 2 lists the yields of gases, carbon conversion and carbon recovery obtained at 690 °C and around 28 Mpa as functions of the Ca/C molar ratio. Runs 3 and 4 as well as runs 6 and 7 demonstrate the reproducibility of experiment. Carbon conversion refers to the sum of carbon fraction in gas phase and that in solid. No determination of liquid was considered in this series of experiment. Regardless of calcium addition, the main combustible gases produced were hydrogen and methane. With more calcium addition up to a Ca/C ratio of 0.6, an increase in the hydrogen yield concurrent with an increase in the carbon conversion was striking; whereas more CO_2 was fixed in the solid. At a Ca/C ratio of 0.6, virtually no CO_2 remained in the gas phase. In the presence of calcium, the yields of methane and ethane appeared to be somewhat larger than those in the absence of calcium. Antal and his collaborators ever made their efforts to produce a hydrogen-rich gas from biomass by supercritical water gasification at 600-650 °C and 30 Mpa [2]. In our study, it was shown that although the proportion of hydrogen in the resultant gas significantly increased, partly because of an increased carbon conversion to hydrogen via reactions (1) and (2), calcium hydroxide had no great effect on the decomposition of methane and ethane into hydrogen.

Table 2. Gas Yields and Carbon Conversion of YL coal with the Addition of $Ca(OH)_2$ (690±4 °C; 28±3 Mpa; holding time at the final temperature, 0 min)

Run No.	Ca/C molar ratio (-)	Gas yield (NL/100g-coal daf) H_2	CO_2	CH_4	C_2H_6	C_3H_8	CO_2 fixed (NL/100g-coal(daf)	Carbon conversion (%)	Carbon recovery (%)
1	0	23.6	18.1	15.8	1.1	nd	-	43.9	86.5
2	0.15	24.0	8.3	15.8	2.2	0.02	16.4	52.1	87.5
3	0.30	29.0	2.4	15.7	2.4	nd	26.1	55.0	86.1
4	0.30	31.6	5.0	15.9	2.6	nd	27.7	60.8	84.6
5	0.45	35.5	0.8	16.6	2.1	nd	30.6	64.4	79.6
6	0.60	38.9	0.1	19.2	2.6	nd	37.0	69.4	82.1
7	0.60	35.4	0.02	18.5	3.2	0.03	40.1	67.6	86.8

nd, not detected (the same as below)

Because the carbon conversion was not as high as expected even with twice amount of $Ca(OH)_2$ added to coal, the reaction was prolonged to examine the gasification of remaining char and the results are listed in Table 3. Surprisingly, in the absence of catalyst, an increase in the carbon conversion was so slight even for prolonging the reaction for 20 min. At a Ca/C ratio of 0.6, hydrogen yield to some degree increased, with the increase of carbon conversion. From these data, we can see that the gasification of residual char was slow even under the supercritical water conditions and with the addition of calcium. We noticed that the molar ratio of H_2 to CO_2 was around 1, half lower than the stoichiometric ratio by reactions (1) and (2). This may be because some hydrogen can be consumed in the formation of CH_4, and also because part of CO_2 can be derived from the volatile of coal.

Table 4 shows the results of the gasification of MW coal and TN coal. It was observed that calcium hydroxide also had an effect on enhancing gasification of these two coals to produce more hydrogen. The three coals used in the study were all young coals which may be better suitable for the gasification in supercritical water. When higher-rank bituminous coals were gasified (not shown here), the carbon and hydrogen yields were relatively low as compared with those obtained for these three coals.

Table 3. Gas Yields and Carbon Conversion of YL Coal Gasified for Different Holding Times at Final Temperature (680±4 °C; 30±2 Mpa).

Run No.	Ca/C molar ratio	Holding time (min)	Gas yeild (NL/100-coal(daf) H_2	CO_2	CH_4	C_2H_6	C_3H_8	CO_2 fixed (NL/100g-coal(daf)	Carbon conversion (%)	Carbon recovery (%)
8	0	0	25.8	18.0	15.7	1.4	nd	-	44.7	86.3
9	0	10	32.3	20.7	14.8	1.4	nd	-	47.2	85.8
10	0	20	36.8	18.9	17.6	1.3	0.02	-	46.0	86.7
11	0.3	0	25.5	0.8	15.4	2.4	nd	30.4	59.4	83.4
12	0.3	10	40.4	6.6	21.1	3.2	nd	27.8	69.6	82.1
13	0.6	10	43.4	0.3	20.9	2.9	0.06	43.8	71.7	87.7
14	0.6	20	46.9	1.8	23.5	2.9	0.02	42.3	74.8	86.5

Table 4. Gas Yields and Carbon Conversion in the gasification of MW coal and TN coal (688 ±2 °C; 28 ±2 °C; holding time, 0 min)

Run No.	Coal sample	Ca/C molar ratio	Gas yield (NL/100-coal(daf) H_2	CO_2	CH_4	C_2H_6	C_3H_8	CO_2 fixed (NL/100g-coal(daf)	Carbon conversion (%)	Carbon recovery (%)
15	MW	0	23.2	17.1	13.3	1.7	0.004	-	47.4	79.8
16	MW	0.45	38.3	0.03	17.5	2.3	0.08	39.7	61.2	87.4
17	TT	0	21.4	14.2	14.5	2.4	0.004	-	49.7	74.7
18	TT	0.45	35.6	0.01	14.1	2.5	0.3	31.2	59.6	79.4

We noticed that the values of carbon recovery shown in Tables 2-4 were not beyond 90%. Despite a small part of carbon loss which was unavoidable in the experimental procedures, the deficient amount of carbon recovery lower than 100% might be mainly due to the excluded carbon fraction in tarry materials. However, some of the filtrates were determined in the amounts of light hydrocarbons, and the partial analysis data and the values of carbon closure through the analysis of light hydrocarbons are given in Table 5. We found that at lower temperatures, the values of carbon closure were still significantly lower than 100% but the balance was enhanced at higher temperatures. At lower temperatures, there obviously existed more BTX, PCX, with more tar that was not determined. In the visible observation, the water solutions separated after filtration were brown in color while the solution obtained at higher temperatures were essentially transparent. An important observation was that calcium oxide had a marked effect on the decomposition of coal in supercritical water. More tarry materials may be formed via promoting hydrolysis and dissolution into dense supercritical water, as well as via preventing the secondary reaction from depolymerization, under the effects of $Ca(OH)_2$ in supercritical water.

Table 5. Carbon Partition into gaseous, liquid and solid products for YL coal.

Experimental conditions FT (°C)	Ca/C (-)	HT (min)	P (Mpa)	Carbon partition (% of total carbon) gaseous CH_4	CO_2	C_2	C_3	BTX	PCX	C_6H_6	solid *	Carbon closure (%)
568	0	13	24	3.3	5.4	0.5	0.1	1.0	1.0	0.1	60.9	72.3
565	0.3	13	25	3.1	0.0	1.2	nd	0.4	1.2	0.2	67.2	74.6
560	0.60	12	28	4.2	0.0	1.5	0.4	0.4	1.6	0.0	68.3	76.3
680	0	20	32	12.6	14.7	2.3	0.1	0.0	0.7	0.0	57.8	88.3
683	0.6	20	29	17.0	0.1	4.7	0.1	0.0	0.6	0.0	63.2	88.0

*, including carbon as $CaCO_3$ and organic carbon

Figure 1 displays the relation of CO_2 sorption and calcium utilization with Ca/C molar ratio. In the case of almost complete retention of CO_2, the value of calcium utilization was 50-60%. When prolonging the reaction, carbon dioxide was not effectively captured by remaining calcium, as illustrated in Figure 2. However, it remained doubtful how much the CO_2 could possibly be captured during cooling stage.

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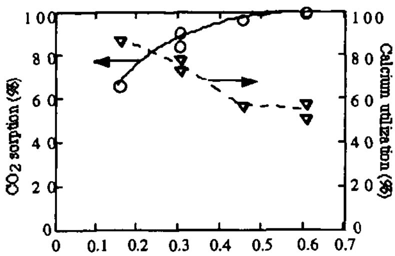

Figure 1. CO_2 sorption and calcium utilization the amount of $Ca(OH)_2$ added (690 °C, 28 Mpa, 0 min holding time).

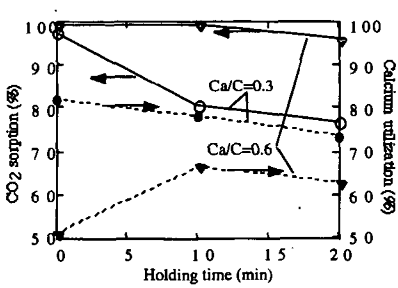

Figure 2. CO_2 sorption and calcium utilization with holding time at varying Ca/C molar ratio (680 °C, 30 Mpa).